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Title: *Measurements of Ultraviolet Absorption Cross Sections of NO_2 at Various Pressures and Temperatures*

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Contents

1 Abstract

An account is given of progress towards the measurements of absolute, ultra violet cross sections of NO_2 during the ten-month period 10/1/93–7/31/94. The accomplishments include: *(a)* construction of an absorption cell; *(b)* construction of vacuum system; *(c)* the assembly of an optical system including focusing of a 6.65 m spectrograph; *(d)* obtaining high resolution photographic spectra of NO_2 in absorption; and *(e)* the first measurements of cross sections of NO_2 at 295 K. The high resolution absorption spectrum of NO_2 has been obtained from National Research Council of Canada [Douglas and Huber, Can. J. Phys. **43**, 74 (1965)]. The high resolution cross sections of NO_2 at 295 K have been measured photoelectrically in the wavelength region 390–452 nm. No pressure dependency has been observed. The absolute cross section scale agrees with published values, but there are large wavelength shifts in earlier works.

2 Progress Report for the Period 10/1/93-7/31/94

2.1 High resolution photographic works

Douglas and Huber [1965] photographed and investigated the absorption bands of NO_2 in the wavelength region 370-460 nm with the third order of a 10-m Eagle spectrograph. Dr. Huber kindly transferred to us all photographic plates of NO_2 from the National Research Council, Canada to the Harvard-Smithsonian Center for Astrophysics (CfA). All plates have now been safely moved to the CfA for investigations. The NO_2 bands in region 430-460 nm consists of many vibronic structures which have never been presented by any of the previous workers on cross sections. These should be measured with very high wavelength resolution.

2.2 Construction of an absorption cell

The absorption cell for working on NO_2 was designed with a variable pathlength as shown in Fig. 1. The cell is made from stainless steel tubes and consists of an outer tube (3″ OD) surrounding two inner tubes (1″ OD) each closed with silica windows. The outer tube is placed in a styrene foam box, which can hold a liquid at constant temperature. The inner tubes can be evacuated to prevent condensation forming on the windows at low temperature. For the cross section measurements of NO_2, the pathlength was set at 42.5±01 cm. NO_2 in the cell was maintained at the same temperature as the liquid (*e.g.* ice water) in the insulated box.

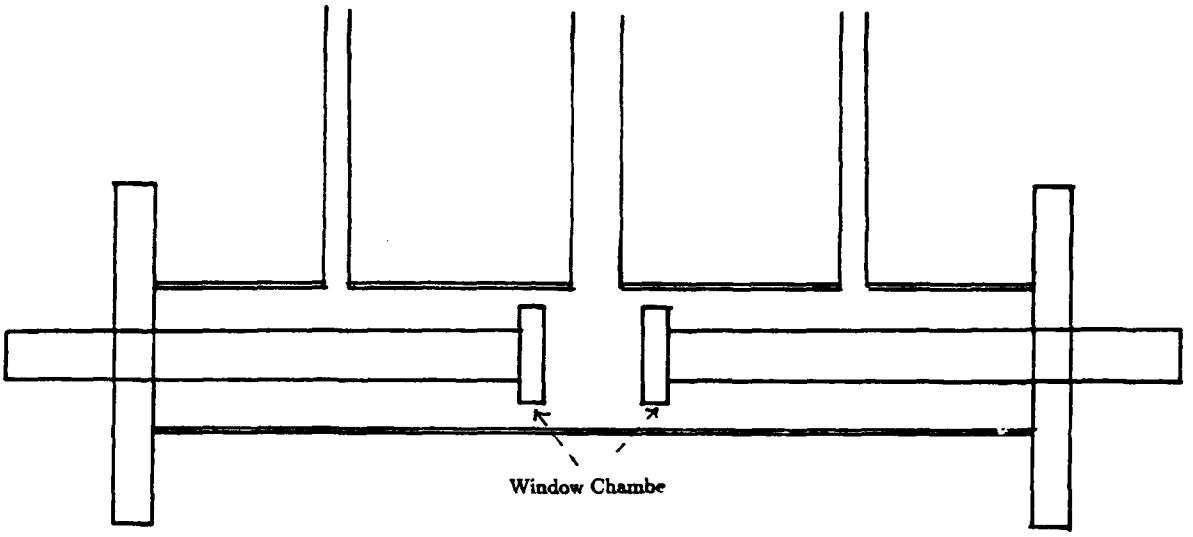

Figure 1: Schematic diagram of the absorption cell. The pathlength can be varied by changing the separation between the inner tubes.

2.3 Vacuum system and purification of NO_2

The vacuum system was constructed with Pyrex glass and evacuated with a Mercury diffusion pump. The NO_2 (Matheson Ltd) was stored in part of the vacuum system, and, to eliminate any contamination of N_2, O_2, and NO, was pumped down at liquid nitrogen temperature. The other impurities of NO-complexes were removed by distillation until only white solid NO_2 material is observed at liquid nitrogen temperature. The purified gas is stored in a blackened flask.

2.4 Focus and alignment of the 6.65 m spectrometer

The spectrograph was focused with incident angle, 11°20′, which covered the wavelength region 368-458 nm in photographic mode. As shown in Fig. 2, the absorption cell was directly attached to the slit chamber of the spectrometer. A hollow cathode lamp (Ne-Fe) was used for wavelength calibration, and a tungsten lamp, operated at 12 V ac, used as the background source. A lens was used to make an image of the light source on the slit. We recorded photon counts in the range 28,000–78,000/sec as background intensity with a 20μm slitwidth in the wavelength region 390–452 nm.

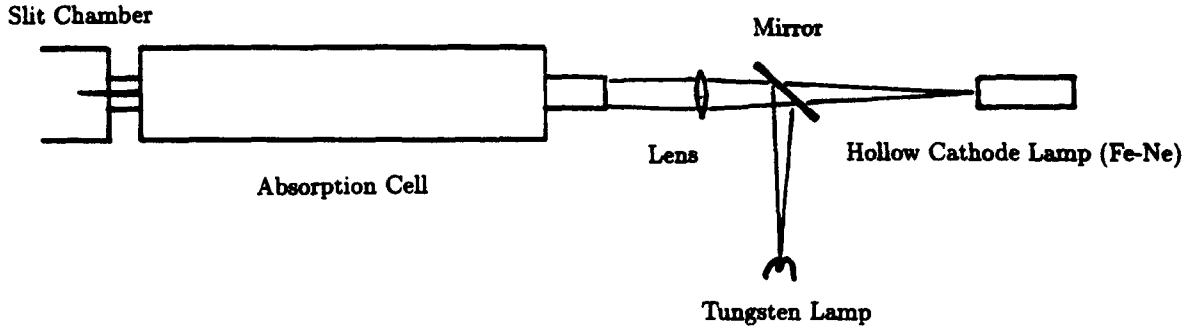

Figure 2: Schematic diagram of optical arrangement. An image of the source is formed on the entrance slit of the spectrometer by a lens.

2.5 Cross section measurements of NO_2

At a scanning speed of 6.4 mm/min, the 7.3 nm range is covered in ~9 min. Data were taken every 0.118 sec for every 15mÅ (0.074 cm^{-1}). In each scan range, we ran the hollow cathode spectrum for wavelength calibration and the accuracy of wavelength was 0.02 Å. For NO_2 absorption measurements, we record the background intensity at the start wavelength, then fill with the NO_2 gas, scan for about 9 minutes, pump out the gas, and again record the background intensity. The linear interpolation of these two measurements are used to set the background level; the background intensity varies linearly with wavelength. The pressures of NO_2 were selected as 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 Torr. The cross sections of NO_2 dimers should be pressure dependent, and we expected to be able to notice the influence of dimers by comparing cross sections with pressure.

The measured cross sections of NO_2 are shown in Fig. 3 in the wavelength 390-450 nm, with a pressure of NO_2 of 2.0 Torr at 295 K. Most of "noisy" structures are real, and the detail structures appear in the photographic spectra from Douglas and Huber [1965].

Our spectrum is compared with those of Hall and Blacet [1952] and Schneider *et al.* [1986] in the wavelength range, 425-455 nm, in Fig. 4. The scale of our cross sections agrees well with both. However the cross sections of Hall and Blacet are shifted to shorter wavelength by almost 1 nm. On the other hand, the Schneider *et al.* values agree with ours very well below 435 nm, but there is a gradual wavelength shift above 440 nm. By 450 nm the shift approaches 0.5 nm.

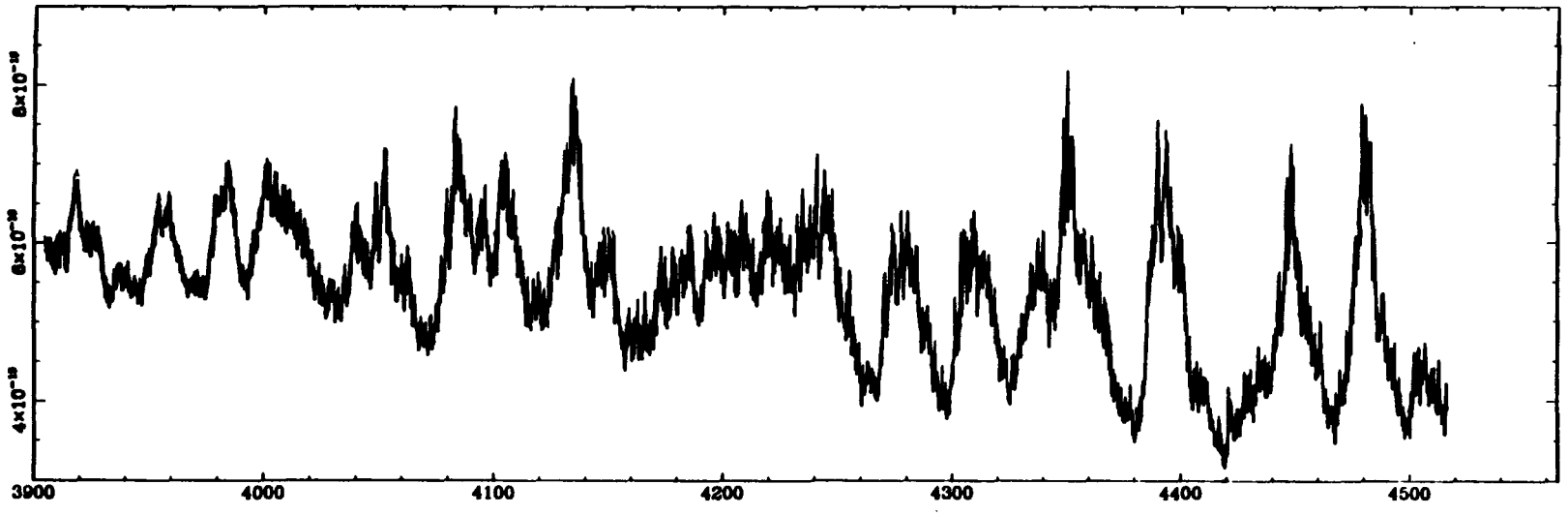

Figure 3: Cross sections of NO_2 at 295 K with 2.0 Torr of NO_2 in the absorption cell. The cross sections are obtained at 0.08cm^{-1} step.

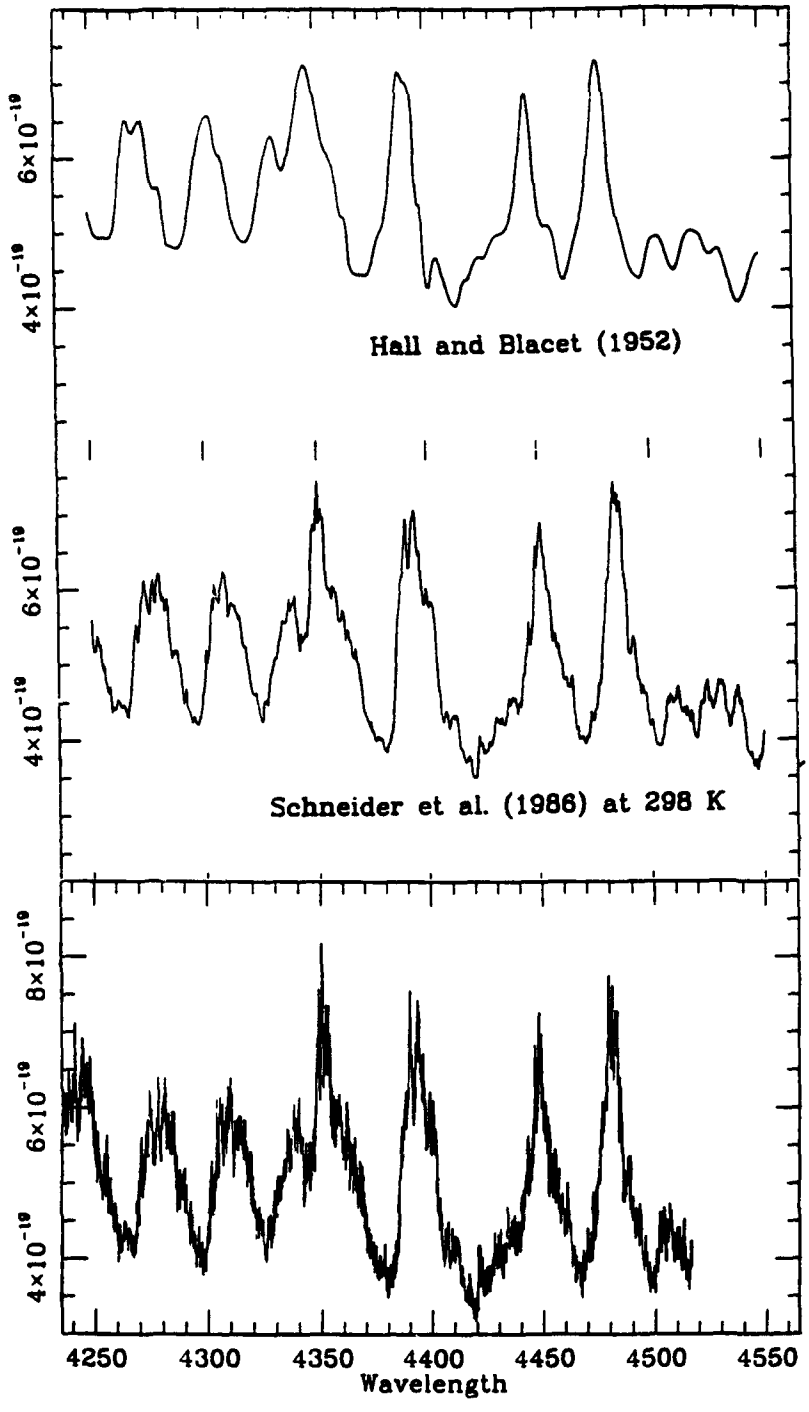

Figure 4: Comparison of our cross sections of NO_2 with previous works. The spectrum of Hall and Blacet [1952] (top) is shifted to shorter wavelength. The values of Schneider *et al.* [1986] (middle) agree very well with ours but there is a wavelength shift above 440 nm.

Our measured cross sections were obtained with a wide range of pressures, (0.5-3.0 Torr), and in this pressure range, agree very well within experimental uncertainty (see Fig. 5). The cross sections are determined assuming a column density of pure NO_2. The fact that there was no pressure dependence in our cross section measurements indicated that there were no dimer absorptions in this wavelength region (as known previously).

The band at 391 nm has been analysed by Douglas and Huber [1965]. We had proposed to use the band oscillator strength of this band to monitor NO_2 density. However, we found the band was too weak to be used for monitoring NO_2 density for low temperature work.

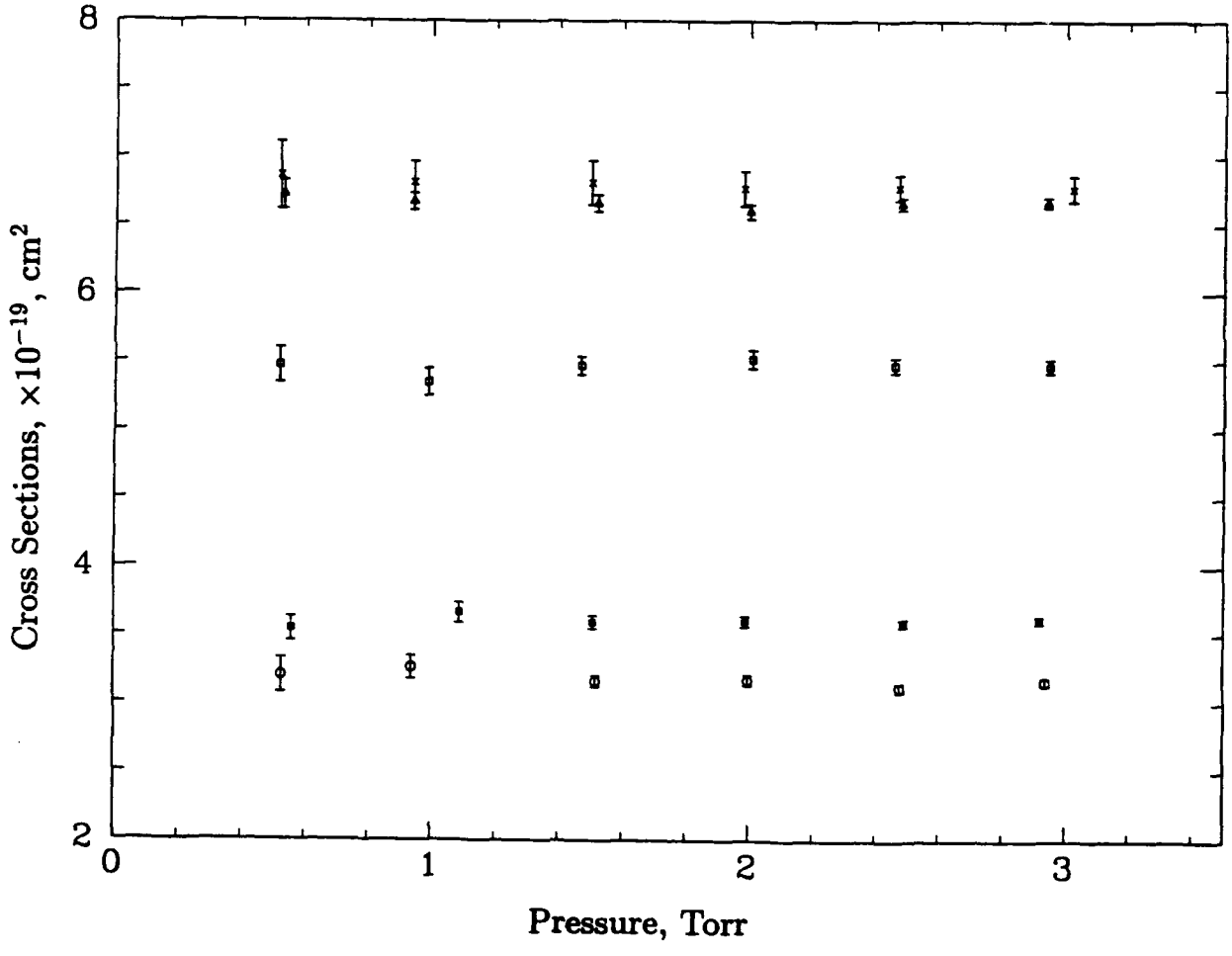

Figure 5: Cross sections of NO_2 at five wavelengths are plotted against pressure. The open squares are at 399.4 nm, triangles at 439.5 nm, open circles at 442.0 nm, crosses at 444.1 nm, and closed squares at 450.0 nm. Part of the error bar is due to the "noisy" structures for 444.1 nm data. No pressure dependency is observed.

3 Proposed work for the Period 10/1/94-9/30/95

We will extend the cross section measurements to slightly longer wavelengths (to 460 nm) and also to shorter wavelengths (to 360 nm) with new settings of the 6.65 spectrometer. The measurements will include those at 235 K and 330 K. Mixed gases (NO_2 in air and/or NO_2 in N_2) will be obtained for the cross section measurements of NO_2 in air and/or N_2. These measurements will be the main efforts in the new year.

4 References

Douglas, A.E. and Huber, K.P. (1965), *The Absorption Spectrum of NO_2 in the 3700-4600 ÅRegion*, Can. J. Phys. **43**, 74-81.

Hall, T.C. and Blacet, F.E. (1952), *Separation of the Absorption Spectra of NO_2 and N_2O_4 in the Range of 2400-5000Å*, J. Chem. Phys. **20**, 1745-1749.

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